Final Report for AOARD Grant FA2386-10-1-4172 (AOARD-10-4172)

30/SEP/2011

Tuning thermal and electrical conductivities in structure-engineered nanowires for high-efficiency thermoelectric devices

01/OCT/2010 – 30/SEP 2011

Name of Principal Investigator: Wooyoung Lee

E-mail address: wooyoung@yonsei.ac.kr

Institution: 262 Seongsanno, Seodaemun-gu, Seoul 120-749, Korea, Department of Materials Science and Engineering, Yonsei University

Phone: +82-2-2123-2834

Fax: +82-2-312-5375

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
30-09-2011

2. REPORT TYPE
FINAL

3. DATES COVERED *(From - To)*
Oct 2010 - Sep 2011

4. TITLE AND SUBTITLE
Tuning Thermal and Electrical Conductivities in Structure-engineered Nanowires for High-efficiency Thermoelectric Devices

5a. CONTRACT NUMBER
FA2386-10-1-4172

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Wooyoung Lee

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Yonsei University, Department of Materials Science and Engineering, Seongsanno 262, Seodaemun-gu, Seoul, Korea

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD, UNIT 45002, APO AP 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD

11. SPONSORING/MONITORING AGENCY REPORT NUMBER
AOARD-104172

12. DISTRIBUTION AVAILABILITY STATEMENT
Apporved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
The search for new materials with enhanced thermoelectric properties continues to be of central importance in thermoelectricity. It has been challenging to increase the thermoelectric figure of merit ($ZT=S2\sigma T/\kappa$) of materials, which determines the efficiency of thermoelectric devices, because the three parameters such as Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ) of bulk materials are inter-dependent. With the development of nanotechnology, ZT of nano-structured materials are predicted to be enhanced by size effects and quantum confinement effects providing the opportunities to control S, σ and κ independently. In particular, for the development of high-efficiency thermoelectric materials, much progress in nanowires has been made to synthesize; 1) high-quality nanowires with a great degree of control on geometry and structures; 2) measurements techniques for studying electronic and thermal transport properties of nanowires; 3) theoretical understanding of phonon transport at nanoscale.

15. SUBJECT TERMS
Nano materials

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	Same as Report (SAR)	21	Wooyoung Lee
unclassified	unclassified	unclassified			**19b. TELEPONE NUMBER** (*Include area code*) +82-2-2123-2834

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI-Std Z39-18

Contents

I. Abstract

The search for new materials with enhanced thermoelectric properties continues to be of central importance in thermoelectricity. It has been challenging to increase the thermoelectric figure of merit ($ZT=S^2\sigma T/\kappa$) of materials, which determines the efficiency of thermoelectric devices, because the three parameters such as Seebeck coefficient (S), electrical conductivity (σ), and thermal conductivity (κ) of bulk materials are inter-dependent. With the development of nanotechnology, ZT of nano-structured materials are predicted to be enhanced by size effects and quantum confinement effects providing the opportunities to control S, σ and κ independently. In particular, for the development of high-efficiency thermoelectric materials, much progress in nanowires has been made to synthesize; 1) high-quality nanowires with a great degree of control on geometry and structures; 2) measurements techniques for studying electronic and thermal transport properties of nanowires; 3) theoretical understanding of phonon transport at nanoscale.

II. Progress summaries

The project has investigated the thermal and electrical conductivities of Bi-based nanowires whose structures are engineered in order to reduce the thermal conductivities without decreasing the electrical conductivity. Numerous previous theoretical and experimental studies suggested the great promise of Bi-based nanowires (Bi, Bi_2Te_3 and BiSb etc) for high thermoelectric figure of merit ZT (ZT is defined as $S^2\sigma T/k$, where S is the Seebeck coefficient, σ is the electrical conductivity, k is the thermal conductivity and T is the absolute temperature).

In this project, high-quality single crystalline nanowires with controlled composition, diameter, crystal structure and embedded nano-sized impurities have been synthesized based on a previously developed stress-induced method (OFF-ON). The study included the investigation of thermal and electrical properties of these structure-engineered nanowires. Thermal and electrical conductivity of individual nanowires have been measured using modified suspended micro-devices with a novel approach for making the electrical and thermal contacts to the nanowires. In addition, the theoretical modeling of phonon transport in nanowires has also been performed by using Monte Carlo distribution method.

a. Interface controllable Bi-Te core/shell nanowire fabrication

b. Thermal transport in individual Bi-Te core/shell nanowire

c. Electrical properties in individual Bi-Te core/shell nanowire

d. Theoretical thermal transport expectation in Bi-Te core/shell nanowire

III. Summary of Accomplishments

1. **“Reduction of lattice thermal conductivity in single Bi-Te core/shell nanowires”** *Adv. Mat*. **23**(30), 3414-3419, **2011. (AOARD-10-4172)**
2. **“Core/shell nanowires: Reduction of lattice thermal conductivity in single Bi-Te core/shell nanowires”** *Adv. Mat*. **23**(30), 3347, **2011. (AOARD-10-4172)**

IV. Tuning thermal and electrical conductivities in structure-engineered nanowires for high-efficiency thermoelectric devices

a. Synthesis of hetero-structure nanowires with high quality single crystalline

The Bi-Te core/shell nanowires were fabricated by the combined use of the on-film formation of nanowires (OFF-ON) method and a simple sputtering technique. First, Bi nanowires were grown from a Bi thin film using the OFF-ON method, which is a spontaneous nanowire growth technique based on the compressive stress arising from the large difference in thermal expansion coefficients of a Bi film (13.4×10^{-6} /ºC) and the SiO_2/Si substrate ((0.5×10^{-6} /ºC)/ (2.4×10^{-6} /ºC)). The Bi thin film was initially deposited onto a thermally oxidized Si (100) substrate at a rate of 32.7 Ǻ/s by radio frequency (rf) magnetron sputtering under a base pressure of 4×10^{-8} Torr. During this Bi thin film deposition, the substrate was kept cool using liquid nitrogen to achieve the small grain morphology that would lead to small-diameter Bi nanowires in the following step. The Bi film subsequently underwent thermal annealing at 260 to 270 ºC for 10 hours to drive the Bi nanowire growth. Once the OFF-ON process was completed, a 30 nm thick Te film was deposited in-situ onto the Bi nanowires at room temperature, using rf magnetron sputtering.

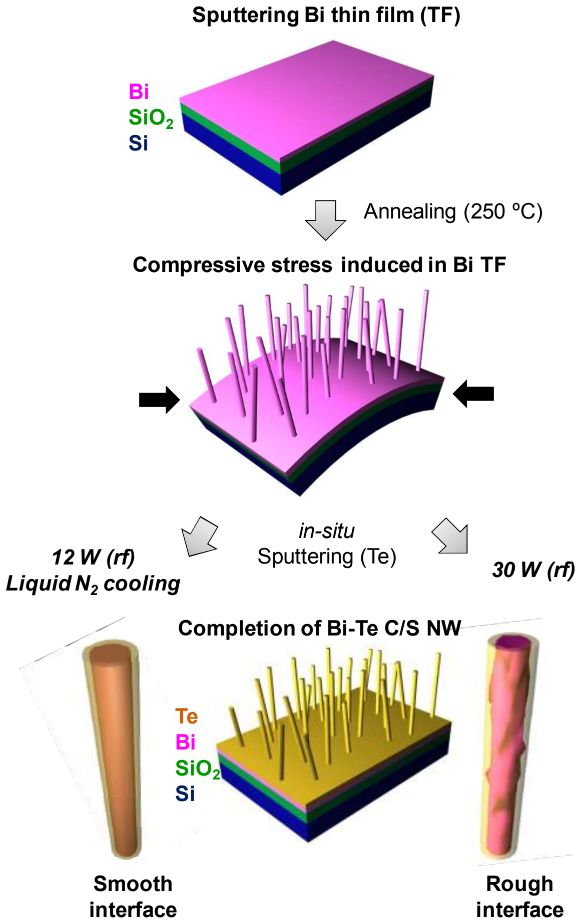

Figure 1. Schematic of interface controllable Bi-Te core/shell nanowire fabrication process

b. Development of interface roughness control method in core/shell nanowires

For smooth interface core-shell nanowire growth, the substrates on which the Bi nanowires have grown is cooled with liquid N2, followed by Te deposition by radio frequency (rf) sputtering with a power of 12 W. Liquid N2 cooling system and low sputtering power can minimize roughness on the surface of Bi nanowires due to suppressed kinetic energy of Te atoms. For rough interface core-shell nanowire growth, no substrate cooling was used, but Te deposition was done with a power of 30 W under ultra-high vacuum (UHV) conditions, which helps physically etch the Bi nanowire surface. The exposure of a suface to energetic particles, i.e. atom bombardment during Te sputtering, can change Bi nanowire surface morphology. High-power Te sputtering onto Bi nanowires is expected to have similar effects. The surface morphology change by incident Te atoms is not likely to be uniform at the nanometer scale, and as a consequence, causes rough surfaces at a comparable length scale. Transmission electron microscopy (TEM) shows the interface of the nanowire, which confirms the presence of the rough interface generated by Te deposition at relatively high power, whereas a Te shell deposited at low power produces a smooth interface. The mean roughness at the rough interfaces of the core-shell nanowires varied from wire to wire, but was typically 5 – 10 nm with a

roughness period of the order of several nanometers. From a high-resolution transmission electron microscopy (HR-TEM) image of a cross-section of a rough interface core/shell nanowire, the existence of the rough surface is clearly seen. Selected area electron diffraction (SAED) patterns reveal that the sputtered Te shell exhibits a low degree of crystallinity or a quasi-amorphous surface, while the Bi core is highly single-crystalline.

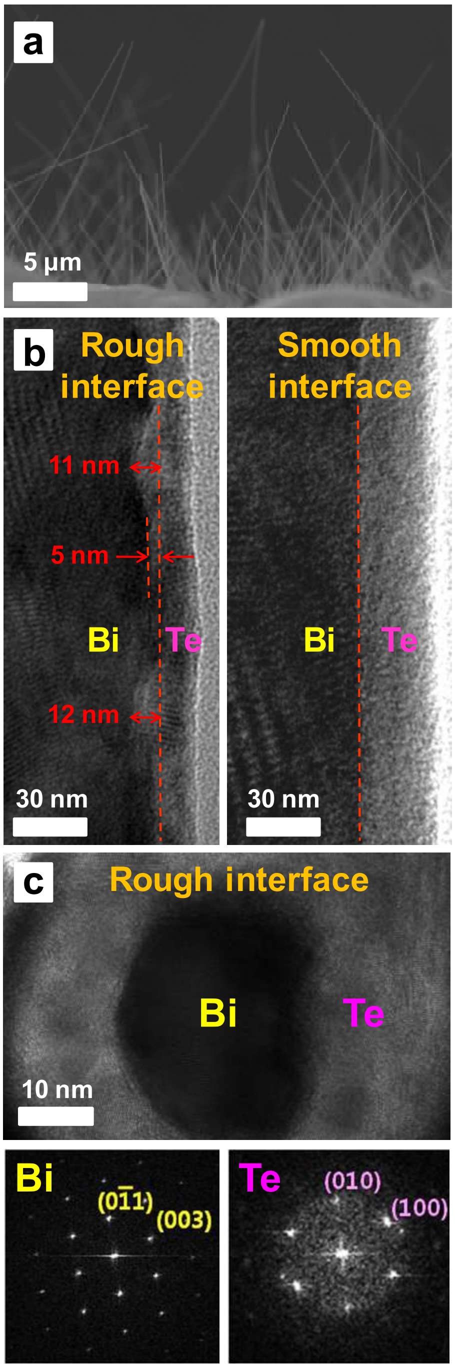

Figure 2. Electron microscopy images of the Bi-Te core/shell nanowire.

c. Characterization of phonon transport in structure-engineered core/shell nanowires

In order to measure the thermal conductivity of an individual Bi-Te core/shell nanowire without thermal conduction through a substrate, we utilized suspended micro-electro-mechanical system (MEMS) devices. Figure 3 shows a SEM image of a suspended MEMS device that consists of two silicon nitride (SiNx) membranes supported by five long beams. A Bi-Te core/shell nanowire was placed between the two suspended membranes by a drop-casting method. Then, to improve thermal contact between the Bi-Te core/shell nanowire and the membranes, a Pt/C composite was locally deposited using a dual-beam focused ion beam (FIB). With negligible radiation loss, the Bi-Te core/shell nanowire should be the only path to conduct heat between the heating membrane and the sensing membrane. The thermal contact resistance was found to be negligible, from a duplicated contact experiment, which revealed that thermal conductivity remained unchanged even after the second thermal contact was made in the vicinity of the first one. Under these conditions, the thermal conductivity of a Bi-Te core/shell nanowire was calculated from the measured thermal conductance, which was determined from temparature changes in the heating and sensing membranes.

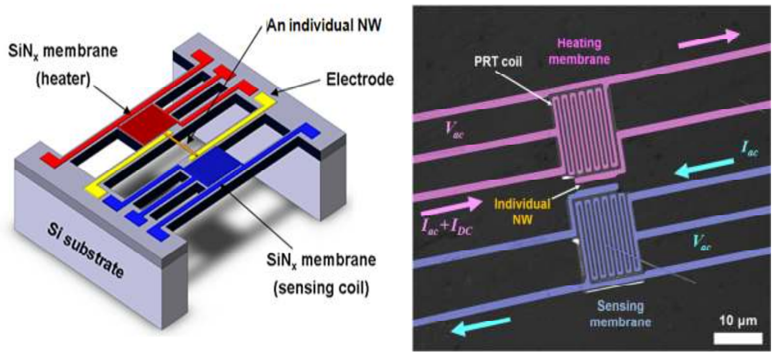

Fig. 3 Measurement of thermoelectric properties using suspended micro-devices

The thermal conductivity, κ_{total}, values for individual rough interface Bi-Te core/shell nanowires with different diameters as a function of temperature (in comparison to smooth interface Bi-Te core/shell and pure Bi nanowires) are shown in Figure 4. The experimental errors are indicated at room temperature, and are associated with noise arising from the electrical measurements and inaccuracies in the measurement of the nanowire area by SEM. For comparison, specific diameters of SI core/shell nanowires (163 nm, 201 nm, and 304 nm) and pure Bi nanowires (178 nm, 203 nm, and 317 nm) were chosen, which are comparable to the diameters of the rough interface core/shell nanowires (170 nm, 230 nm, and 329 nm). We found that the κ_{total} of all nanowires is strongly diameter-dependent, which is attributed to the classical size effect. An interesting general trend for measured κ_{total} is that the κ_{total} values of rough interface core-shell nanowires is two- and fivefold times lower than κ_{total} for SI core-shell and pure nanowires of comparable diameters, respectively.

For example, measured κ_{total} of 1.97 W/m-K (163 nm), 2.12 W/m-K (201 nm), and 3.18 W/m-K (304 nm) in SI core-shell nanowires were larger than measured κ_{total} values of 0.73 W/m-K (163 nm), 0.93 W/m-K (201 nm), and 1.10 W/m-K (304 nm) in rough interface core-shell nanowires. Because few nanometer surface roughness barely changes electrical resistance, there is no significant resistivity change between smooth interface and rough interface core-shell nanowires. Based on this observation, the reduction of κ_{total} can be attributed to the reduction of the lattice thermal conductivity (κ_L) rather than the electronic thermal conductivity (κ_E). κ_L for the 170-nm rough interface core-shell nanowire, for example, was obtained by subtracting κ_E, which can be calculated using the Wiedemann-Franz law, $\kappa_E = L\sigma T$, where L is the Lorenz number, σ is the electrical conductivity and T is the absolute temperature. The Lorenz number for a degenerate system corresponds to 2.44×10^{-8} W-Ω/K^2, and for most conductors it is between 2.2 and 2.7×10^{-8} W-Ω/K^2. Recent studies show that the Lorenz number of a 1-D metal nanowire is found to be smaller than its bulk counterpart and is also reduced with a decrease in carrier concentration that increases resistivity. In this sense, our nanowires, which are 1-D systems and have a higher resistivity than the bulk counterparts, are likely to have a lower Lorenz number than the bulk. For this reason, we have chosen the lower limit of the Lorenz number, 2.2×10^{-8} W-Ω/K^2, since the measured resistivity of the nanowires (1-D system) in this study (10^{-3} – 10^{-4} Ω-cm) is

larger than that of bulk Bi (10^{-5}). In fact, this lower limit (2.2×10^{-8} W-Ω/K^2) has been used in doped Si nanowires with a 1.7×10^{-3} Ω-cm resistivity to calculate the lattice thermal conductivity.

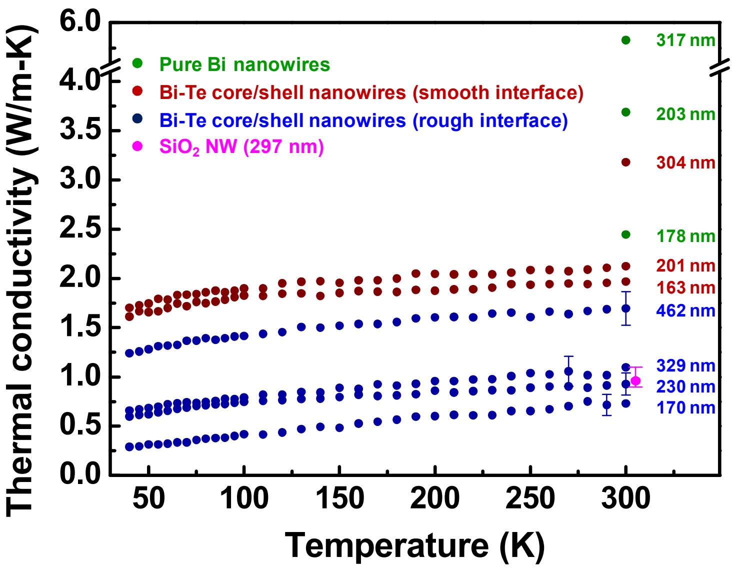

Fig. 4 Thermal conductivities of the Bi-Te core/shell nanowires

We performed electrical transport measurements on the Bi-Te core/shell nanowire to estimate its resistivity. Four-point electrodes were fabricated on the nanowire by the combined use of ICP-RIE and in-situ electrode deposition. The measured I-V curve of a Bi-Te core/shell nanowire with 158 nm diameter is shown in Figure 5, and this curve indicates that ohmic contacts were formed between the nanowire and electrodes. The calculated electrical resistivity is about 2.1 × 10-3 Ω-cm at room temperature.

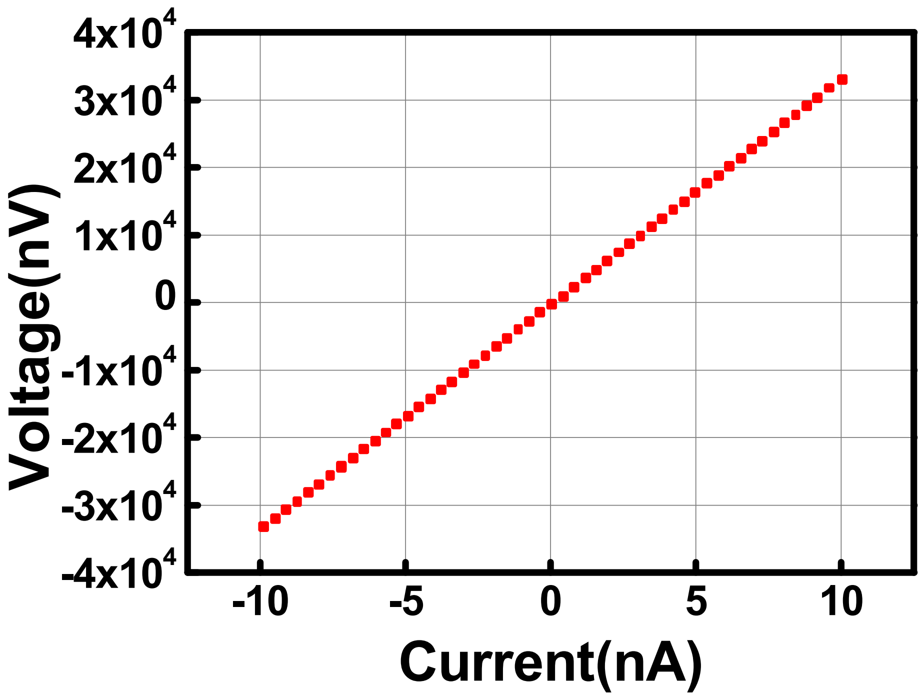

Fig. 5 Electrical resistivity of the individual nanowire at room temperature

d. Theoretical modeling of phonon transport in core/shell nanowires

In a homogeneous nanowire made of a single material, heat transport is governed dominantly by a phonon boundary scattering frequency that is inversely proportional to the wire diameter. Unlike that, a core/shell nanowire has multiple components to be considered when determining the global heat transport.[21-22] In the conventional models of core/shell nanowires with a sharp interface, the effective thermal conductivity can be determined by the individual thermal conductivities and area fractions of core and shell parts, following $[\kappa_{core} \times r_{inner}^2 + \kappa_{shell} \times (r_{outer}^2 - r_{inner}^2)] / r_{outer}^2$,[21] where r_{inner} and r_{outer} are the radius of core and shell, respectively. The core and shell thermal conductivities, κ_{core} and κ_{shell}, become smaller when the layer roughness decreases and diffuse scattering prevails over the specular scattering. We stress that this overly simplistic model completely neglects the influence of any interfacial roughness. Referring to Figure 6, it can be seen that this interface roughness contribution to thermal conductivity reduction is decisive. In the figure, the wire diameter indicates that of Bi component irrespective of heterogeneity of the structure, and the calculated and measured data are represented by the red, green and blue symbols, respectively. The thermal conductivity of the Bi homo-nanowires (red symbols) changes almost linearly with the wire diameter, ranging from 1.6 W/m-K for 98 nm to 5.2 W/m-K for 327 nm. The thermal conductivity

deviation according to the change of diameter of Bi-Te core/shell nanowires ($\Delta\kappa/\Delta d$) is 0.732 [w/m-K]/nm which value reflects the classical size effect in play. Next, we calculated the thermal conductivities of Bi-Te core/shell nanowires (green symbols) with the three differing thicknesses of Bi cores covered with an identical 30 nm thick Te shell, assuming a sharp interface mentioned above. These calculated values fall to about half of those of Bi homo-nanowires at small Bi diameters. This is believed to be caused by the combinative effects of a Te shell with the lower thermal conductivity and the diffuse scattering at the boundary. However, these reduced thermal conductivities are still somewhat higher than the measured values for our Bi-Te core/shell nanowires (blue symbols). This discrepancy between the calculated and our measured values is believed to originate from the rough interface layer. The thermal conductivity deviation according to the change of diameter of Bi-Te core/shell nanowires ($\Delta\kappa/\Delta d$) is merely 0.165 [w/m-K]/nm, which is approximately 4 to 5 fold smaller than those of the Bi homo-nanowires or the calculated core/shell nanowires with a sharp interface. This indicates that the influence of the interface roughness would be sufficient to dominate over the nanowire size effect, underscoring the importance of the interface layer. From these results, we conclude that the rough interface layer must play a pivotal role in suppressing phonon transport, which in turn reduces thermal conductivity significantly.

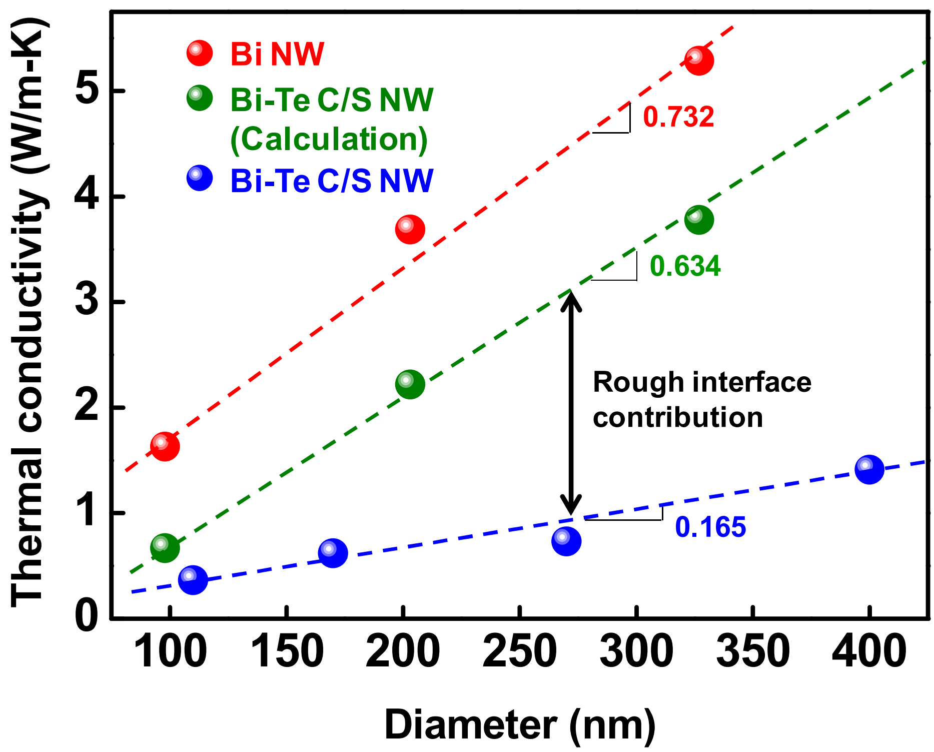

Fig. 6 Heat transport model proposed for explaining the ultra-low thermal conductivity

V. Conclusions

we have investigated the reduction of the lattice thermal conductivity of Bi-Te core/shell nanowires with rough interfaces. A combination of the OFF-ON method and sputtering yields core/shell nanowires with single-crystalline Bi cores and Te shells with a rough interface in between. The thermal conductivity measured for a rough interface Bi-Te core/shell nanowire was smaller than that of a smooth interface Bi nanowire. From these results, it is proposed that the rough interface effectively suppresses phonon contribution to thermal conductivity. Although the values of κ_E and κ_L calculated from measured κ_{total} and ρ may not be precisely correct because the exact Lorenz number is unknown, a qualitative trend of the thermal conductivity reduction in RI core/shell nanowires compared to SI core/shell nanowires demonstrates at least that low-κ can be achieved by this route. Moving forward, an exact mechanism for such thermal conductivity reduction needs to be identified to fully exploit the advantage afforded by this approach.